Synthesis and Electrochemical Properties of Yttrium-doped Spinel $LiMn_{2-y}Y_yO_4$ Cathode Material

Hao Tang, Chuan Qi Feng, Quan Fan, Tai Ming Lei, Ju Tang Sun, Liang Jie Yuan, and Ke Li Zhang*
College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China

(Received April 15, 2002; CL-020326)

Yttrium doped spinel $LiMn_{2-y}Y_yO_4$ with single phase was synthesized and characterized. The data of the XRD show that the limit for Y solubility is $y \leq 0.02$. The beneficial effect of Y is evident by way of improved cyclability. The electrode of $LiMn_{1.98}Y_{0.02}O_4$ shows excellent electrochemical properties with a first discharge capacity of 118 $mA \cdot h \cdot g^{-1}$ and retaining 98% of the initial capacity after 100 cycles at the current rate 0.2 C.

The spinel $LiMn_2O_4$ is regarded as one of the best-known compounds used as an insertion cathode in 4 V rechargeable lithium batteries due to their low cost, abundance, and non-toxicity compared with layered oxide such as $LiCoO_2$ and $LiNiO_2$.[1–3] The capacity of this cathode, however, decreases with cycling in the 4 V range.[4] The capacity fade in spinel $LiMn_2O_4$ is described as due to a J–T effect of Mn^{3+} and the weaker Mn–O bond in octahedron. This capacity drop has been addressed by exploring alternatives to classic ceramic synthetic method[5,6] and by doping the spinel with various elements in order to improve its stability against cycling.[7,8] Some work has also been done for doping spinel with Y^{3+}, whose radius is larger than that of the Mn^{3+}. But there is no report so far on yttrium-substituted spinel compounds with pure phase having energy capacity and cycle life behavior comparable to other well-known substituted spinels. However, the work of doping spinels with yttrium and other rare earth elements is still attractive and interesting. Recently, Wan[11] has successfully synthesized the rare earth elements (La, Pr, and Sm) doped spinels with smaller dopants. The doped spinels have single phase and show excellent electrochemical properties. These results indicate that the substitution with large cations under suitable conditions can also largely improve the cyclability of the $LiMn_2O_4$ spinel.

In this work, we have attempted to synthesize pure-phase yttrium doped spinels with smaller dopants by using rheological phase reaction method and to investigate their electrochemical properties for lithium ion intercalation reaction.

The rheological phase reaction method is a process of preparing compounds or materials from solid-liquid rheological mixtures. That is, the solid reactants were fully mixed in a proper molar ratio, made up by adding a proper amount of water or other solvent to a solid-liquid rheological body in which the solid particles and liquid substance were uniformly distributed. Then after reaction under suitable conditions, the product was obtained. Under the solid-liquid rheological state, many substances have new reaction properties, which can be seen in our early work.[12–14]

The complex $LiMn_{2-y}Y_yO_4$ studied in this work were prepared using the rheological phase reaction method. The $CH_3COOLi \cdot 2H_2O$, $(CH_3CO_2)_2Mn \cdot 4H_2O$, and Y_2O_3 were mechanically mixed in proper mole ratios, then add a proper quantity of citric acid (the amount equals to the mole sums of the total metal ions). After the powders were mixed homogeneously, a proper quantity of water was added. A solid-liquid rheological body was made by slightly milling the solid and liquid mixtures. Then a precursor was obtained from the solid-liquid rheological body in a open container at 70–90 °C for 8–10 h. The spinel $LiMn_{2-y}Y_yO_4$ was obtained by thermal decomposition of the precursors at 700 °C for 12 h in air.

Powder X-ray diffraction patterns using Cu Kα radiation was employed to identify the crystalline phase of prepared powders. Coin cells were fabricated using lithium foil as the anode, spinel powders mixed with 12% acetylene black and 8% polytetrafluoroethylene(PTFE) as the cathode and 1M $LiClO_4$/PC : DMC(1 : 1) as the electrolyte. The charge-discharge cycle was performed at 0.2C rate between 3.6 and 4.4 V.

Figure 1 shows the XRD spectra for the both undoped and various yttrium doped $LiMn_2O_4$ spinel. All the synthesized compounds show sharp peaks indicating a high degree of crystallinity. The Y doped spinels of $y > 0.02$ showed small impurity lines, due to YMn_2O_5 indicating that the solid solubility of Y is about 2 mol%. Although the dopant concentrations were low, ranging from 0.5 mol% to 2 mol%, the effect of the presence of Y^{3+} was well reflected in the structural properties of the host. The cubic lattice constant values of prepared spinels decrease with increase in the doping level yttrium ($y \leq 0.02$), showing that the substitution plays its role in reducing the cubic spinel size. These results were well reflected in the electrochemical properties of the systems. It is hard to explain why the lattice constant of the spinel decreases since the radius of Y^{3+} is larger than that of the Mn^{3+}. But this decrease was also observed by Wan et al.[11] when they attempted to substitute other rare earth elements into spinel. This phenomenon is abnormal but very interesting. And now, the work is in process to make further studies.

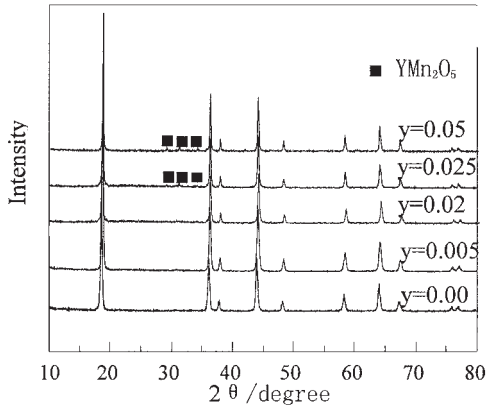

Figure 1. XRD of $LiMn_{2-y}Y_yO_4$ powders ($y = 0.0, 0.005, 0.02, 0.025, 0.05$).

Cycling performance of the undoped as well as the various doped compositions of $LiMn_2O_4$ are shown in Figure 2. All the Y doped spinel show lower initial capacity than undoped $LiMn_2O_4$

but much better cyclability. Even for the smaller dopant of $y = 0.005$, the cyclability is attractive with retaining about 90% of the initial discharge capacity after 100 cycles. With the increase of the doping level yttrium, the initial capacity decreases but the cyclability increases, and the compound $LiMn_{1.98}Y_{0.02}O_4$ gets the best cycle stability. When $y > 0.02$, with the dopant concentration increasing, both of the initial capacity and cyclability are decreasing due to the impure phase. And when $y = 0.05$, the material has only 92 mA·h·g^{-1} initial discharge capacity with retaining 84% after 100 cycles. Selected charge-discharge curves for the sample $LiMn_{1.98}Y_{0.02}O_4$ are shown in Figure 3. It exhibits two distinct potential plateaus near 4 and 4.16 V and the polarization of the electrode is almost constant during cycling. Although the electrode delivers a capacity of 118 mA·h·g^{-1}, it shows excellent cycle stability and retains 98% of the initial capacity after 100 cycles at 0.2C rate. This performance is good and competes with that of conventional materials such as $LiCoO_2$ and $LiNi_{1-x}Co_xO_2$.

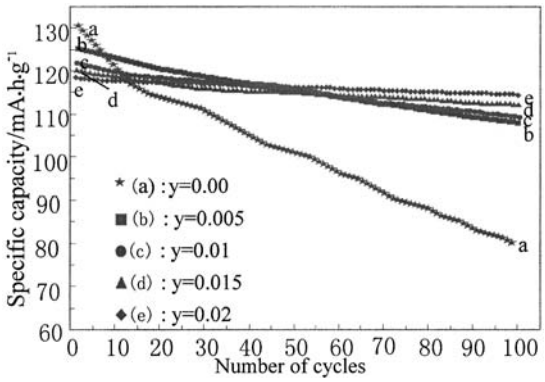

Figure 2. Variation of capacity with cycle number for positive electrode materials $LiMn_{2-y}Y_yO_4$ ($y = 0.0$–0.02).

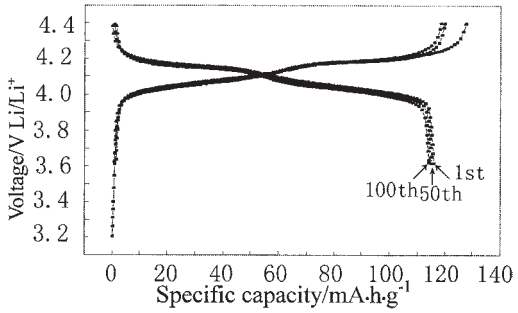

Figure 3. Charge-discharge curves for $LiMn_{1.98}Y_{0.02}O_4$/Li cell in voltage: 3.6–4.4 V.

From the results of the experiments, we can draw the conclusions that the Rheological Phase Reaction method offers a new and efficient way to prepare compounds and materials. And the prepared $LiMn_{2-y}Y_yO_4$ compounds show the excellent electrochemical properties. When $y = 0.02$, the capacity and stability of the cathode materials reached to the best states, its initial capacity reached to 118 mA·h·g^{-1}, after 100 cycles, its capacity was still around 116 mA·h·g^{-1}, with nearly 100% reversible efficient. It seems that the new positive material is still suitable to reinsert lithium ion. We think that the relative stability of parent spinel and yttrium doped spinel could be probably conceived through comparing the standard Gibbs energies of formation (ΔG_f^o) at 298 K of Mn_2O_3 and Y_2O_3, which lie at -881 and -1816.6 kJ/mol, respectively. These values lead to the conclusion that yttrium could confer higher stability to the spinel, which in turn increases the electrochemical cycleability. In addition, when yttrium is substituted into the spinel, the stronger bond Y–O (compared to bond Mn–O) can also improved the stability of the structure. Currently, work is in process to further understand the refined structure of the doped spinels and the relations between the structure and the cycle stability.

This work was supported by The National Nature Science Foundation of China (No. 20071026).

References

1 T. Ohuzuku, M. Kitagawa, and T. Hirai, *J. Electrochem. Soc.*, **137**, 760 (1990).
2 W. J. Macklin, R. J. Neat, and R. J. Powell, *J. Power Sources*, **34**, 39 (1991).
3 D. Guyomard and J. M. Tarascon, *Solid State Ionics*, **69**, 222 (1994).
4 A. Momchilov, V. Manev, A. Nassalevska, and A. Kozawa, *J. Power Sources*, **41**, 305 (1993).
5 P. Barboux, J. M. Tarascon, and F. K. Shokoohi, *J. Solid State Chem.*, **94**, 18 (1991).
6 Y. Xia and M. Yoshio, *J. Electrochem. Soc.*, **143**, 825 (1996).
7 L. Guohua, H. Ikuta, T. Uchida, and M. Wakihara, *J. Electrochem. Soc.*, **143**, 178 (1996).
8 P. Arora, B. N. Popov, and R. E. White, *J. Electrochem. Soc.*, **145**, 807 (1998).
9 A. D. Robertson, S. H. Lu, W. F. Averill, and W. F. Howard, *J. Electrochem. Soc.*, **144**, 3500 (1997).
10 H. J. Choi, K. M. Lee, and J. G. Lee, *J. Power Sources*, **103**, 154 (2001).
11 C. Y. Wan, Y. N. Nuli, and Z. Y. Jiang, *Chem. J. Chinese University*, **23**, 126 (2002).
12 J. T. Sun, X. Wei, L. J. Yuan, K. L. Zhang, and Q. Y. Wang, *Mater. Sci. Eng., B*, **64**, 157 (1999).
13 K. L. Zhang, M. K. Jia, H. Tang, J. B. Yuan, L. J. Yuan, and J. T. Sun, *J. Wuhan University (Natural Science Edition)*, **47**, 657 (2001).
14 Y. Zhang, K. L. Zhang, M. K. Jia, H. Tang, J. T. Sun, and L. J. Yuan, *Chem. Lett.*, **2002**, 176.